

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number  
**WO 03/040422 A1**

(51) International Patent Classification<sup>7</sup>: C22C 45/10, B22D 23/06

(74) Agent: OLIVER, Eric; Dickstein Shapiro Morin & Os-  
hinsky LLP, 2101 L Street NW, Washington, DC 20037-  
1526 (US).

(21) International Application Number: PCT/US02/35436

(22) International Filing Date:  
5 November 2002 (05.11.2002)

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,  
VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60330,947 5 November 2001 (05.11.2001) US

(71) Applicant (*for all designated States except US*): JOHNS  
HOPKINS UNIVERSITY [US/US]; Office of Technol-  
ogy Transfer, W-407 Wyman Park Center, 3400 N. Charles  
Street, Baltimore, MD 21218-2695 (US).

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,  
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): HUFNAGEL, Todd,  
C. [US/US]; 9 Greenridge Road, Lutherville, MD 21093  
(US). OTT, Ryan, T. [US/US]; 6413 Doral Drive, Apt. B,  
Baltimore, MD 21209 (US). FAN, Cang [CN/US]; 6920  
Donachie Road, Apt. #510, Baltimore, MD 21209 (US).  
KECSKES, Laszlo [US/US]; 214 Heater Way, Havre de  
Grace, MD 21078 (US).

Published:

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

P, A

WO 03/040422 A1

(54) Title: ALLOY AND METHOD OF PRODUCING THE SAME

(57) Abstract: In accordance with a preferred embodiment of the invention, an alloy or other composite material is provided formed of a bulk metallic glass matrix with a microstructure of crystalline metal particles. The alloy preferably has a composition of  $(X_aNi_bCu_c)_{100-a-c}Y_dAl_e$ , wherein the sum of a, b and c equals 100, wherein  $40 \leq a \leq 80$ ,  $0 \leq b \leq 35$ ,  $0 \leq c \leq 40$ ,  $4 \leq d \leq 30$ , and  $0 \leq e \leq 20$ , and wherein preferably X is composed of an early transition metal and preferably Y is composed of a refractory body-centered cubic early transition metal. A preferred embodiment of the invention also provides a method of producing an alloy composed of two or more phases at ambient temperature. The method includes the steps of providing a metastable crystalline phase composed of at least two elements, heating the metastable crystalline phase together with at least one additional element to form a liquid, casting the liquid, and cooling the liquid to form the alloy. In accordance with a preferred embodiment of the invention, the composition and cooling rate of the liquid can be controlled to determine the volume fraction of the crystalline phase and determine the size of the crystalline particles, respectively.

## ALLOY AND METHOD OF PRODUCING THE SAME

[0001] This application claims priority to U.S. provisional application 60/330,947, filed November 5, 2001, which is incorporated herein in its entirety.

## GOVERNMENT INTEREST

[0002] The invention was made with government support under Grant No. DE-FG02-98ER45699 awarded by the Department of Energy and Grant No. DAAD-19-01-2-0003 awarded by the U.S. Army Research Laboratory. The government has certain rights in the invention.

## BACKGROUND

[0003] Bulk metallic glasses ("BMG") have generated interest as structural materials due to their unique mechanical properties, which include high strength and large elastic elongation. Metallic glasses, unlike conventional crystalline alloys, have an amorphous or disordered atomic-scale structure that gives them unique properties. For instance, metallic glasses have a glass transition temperature ( $T_g$ ) above which they soften and flow. This characteristic allows for considerable processing flexibility. Known metallic glasses have only been produced in thin ribbons, sheets, wires, or powders due to the need for rapid cooling from the liquid state to avoid crystallization. A recent development of bulk glass-forming alloys, however, has obviated this requirement, allowing for the production of metallic glass ingots greater than one centimeter in thickness. This development has permitted the use of metallic glasses in engineering applications where their unique

mechanical properties, including high strength and large elastic elongation, are advantageous.

[0004] A common limitation of conventional metallic glasses, however, is their tendency to experience plastic deformation in narrow regions called shear bands. This localized deformation increases the likelihood that metallic glasses will fail in an apparently brittle manner in any loading condition (such as tension) where the shear bands are unconstrained. As a result, monolithic metallic glasses typically display limited plastic flow (0-4% under uniaxial compression) at ambient or room temperature. This lack of widespread plastic deformation results in low toughness. Toughness is a critical parameter in any structural material.

#### SUMMARY

[0005] In accordance with a preferred embodiment of the invention, an alloy or other composite material is provided formed of a bulk metallic glass matrix with a microstructure of crystalline metal particles. The alloy preferably has a composition of  $(X_aNi_bCu_c)_{100-d}Y_dAl_e$ , wherein the sum of a, b and c equals 100, wherein  $40 \leq a \leq 80$ ,  $0 \leq b \leq 35$ ,  $0 \leq c \leq 40$ ,  $4 \leq d \leq 30$ , and  $0 \leq e \leq 20$ , and wherein preferably X is composed of an early transition metal and preferably Y is composed of a refractory body-centered cubic early transition metal.

[0006] A preferred embodiment of the invention also provides a method of producing an alloy composed of two or more phases at ambient temperature. The method includes the steps of providing a metastable crystalline phase composed of at least two elements, heating the metastable crystalline phase together with at least one additional element to form a liquid, casting the liquid, and cooling the liquid to form the alloy. In accordance with a preferred embodiment of the invention, the composition and cooling rate of the liquid can be controlled to determine the volume fraction of the crystalline phase and determine the size of the crystalline particles, respectively.

[0007] These and other advantages and features of the invention will be more readily understood from the following detailed description of the invention that is provided in connection with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 is a graph indicating x-ray diffraction patterns for alloys constructed from composites in accordance with an embodiment of the invention.

[0009] Figure 2 is an optical micrograph of an alloy constructed in accordance with an embodiment of the invention.

[0010] Figure 3 is a graph plotting the fraction of the crystalline phase and the tantalum concentration in an amorphous matrix as a function of the overall tantalum content in an alloy constructed in accordance with an embodiment of the invention.

[0011] Figure 4 is a high resolution transmission electron microscope image of the amorphous matrix of Figure 3.

[0012] Figure 5 is a graph indicating thermal properties of alloys constructed from composites in accordance with an embodiment of the invention.

[0013] Figure 6 is a graph indicating an x-ray diffraction pattern for an annealed alloy constructed from a composite in accordance with an embodiment of the invention.

[0014] Figure 7 is a graph indicating x-ray diffraction patterns for annealed alloys constructed from composites in accordance with an embodiment of the invention.

[0015] Figure 8 is a graph indicating mechanical properties for an alloy constructed from a composite in accordance with an embodiment of the invention.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0016] In accordance with a preferred embodiment of the invention, a new type of bulk metallic glass ("BMG") matrix composite alloy has been prepared using an in situ processing method. Preferably, this BMG matrix composite alloy is a two-phase alloy including a metallic glass matrix and a microstructure having crystalline particles embedded in the metallic glass matrix. The volume fraction of the crystalline particles may be controlled through control of the composition of the BMG matrix composite alloy. Alternatively, the size of the crystalline particles may be controlled through control of the cooling rate or by heat treating the precursor materials.

[0017] In a preferred embodiment, the BMG matrix composite alloy has a general composition (in atomic percentage) of  $((X)_aNi_bCu_c)_{100-d-e}Y_dAl_e$ . In this general composition,  $a + b + c$  equals 100, where  $40 \leq a \leq 80$ ,  $0 \leq b \leq 35$ ,  $0 \leq c \leq 40$ ,  $4 \leq d \leq 30$ , and  $0 \leq e \leq 20$ , where X is composed of an early transition metal and Y is composed of a refractory body-centered cubic early transition metal. Preferably,  $40 \leq a \leq 65$ ,  $0 \leq b \leq 10$ ,  $0 \leq c \leq 20$ ,  $4 \leq d \leq 30$ , and  $0 \leq e \leq 15$ . X may, for example, be Zirconium (Zr), Hafnium (Hf), or Titanium (Ti), any of which may be substituted for each other in any proportion. Y, for example, may be tantalum (Ta), which may be replaced by another refractory body-centered cubic (bcc) early transition metal such as vanadium (V), niobium (Nb), molybdenum (Mo), tungsten (W), etc. Any variety of materials or compositions may be used. The crystalline particles may be, for example, formed by tantalum alone or a combination of tantalum and zirconium. Further, in a preferred embodiment, the crystalline particles may be a crystalline solid solution having a composition of greater than eighty percent tantalum. The average grain size of the crystalline particles is preferably between about 0.1 microns and about 100 microns, and preferably, between about 10 microns and about 50 microns.

[0018] In accordance with a preferred embodiment, a homogeneous melt from one of these alloys is cast in such a way as to cool the melt at a moderately high cooling rate, preferably less than 1000 K/s. As a result, a microstructure is produced including a bulk metallic glass matrix surrounding homogeneously dispersed, micron-scale equiaxial crystalline particles rich in a refractory body-centered cubic (bcc) metal, such as tantalum (Ta), vanadium (V), niobium (Nb), molybdenum (Mo), or tungsten (W). In accordance with a preferred embodiment, the volume fraction of the particles can be controlled by

varying the composition of the alloy (e.g., increasing with increasing d), and their size and spacing can be controlled by varying the cooling rate (e.g., decreasing with increasing cooling rate). The matrix may be a metallic glass, and it may be partially or fully crystalline or partially or fully quasi-crystalline.

[0019] The BMG matrix composite alloy of a preferred embodiment of the invention exhibits, under loading, a significant increase in the plasticity experienced by the sample in quasi-static uniaxial compression than conventional metallic glasses. Additionally, the BMG matrix composite alloy retains the characteristic properties of a metallic glass such as a glass transition temperature, a high yield strength (e.g., about two GPa), and a large elastic elongation (e.g., about two percent). Like monolithic metallic glasses, at room temperature the BMG matrix composite alloy deforms by localized plastic deformation in shear bands. Unlike monolithic metallic glasses, however, the presence of the second-phase particles (Ta, V, Nb, Mo, W, etc.) promotes the formation of new shear bands in the BMG matrix composite alloy, while also inhibiting the propagation of existing shear bands. The result is a distribution of plastic strain, forming a composite with significantly enhanced ductility. Preferably, the plastic strain to failure in uniaxial compression at ambient temperature is greater than five percent and up to 15 percent, and the plastic strain to failure in uniaxial tension at ambient temperature is greater than two percent.

[0020] In accordance with a preferred embodiment of the invention, a BMG matrix composite alloy can be made by a low cost in situ method directly from the melt. The BMG matrix composite alloy can be produced by vacuum arc melting an ingot of the

desired composition, followed by casting into a copper mold, or by any similar technique (such as die casting) that provides sufficiently rapid cooling of the melt. The crystalline particles may be obtained through a variety of methods, such as, for example, precipitating them from a supersaturated solid solution prior to melting and solidification of the composite alloy, precipitating them from a liquid alloy during cooling, precipitating them from a supercooled liquid alloy during cooling, or precipitating them from a solid alloy by annealing.

### EXAMPLES

[0021] To illustrate implementations of one or more embodiments of the invention, the following examples are provided. An exemplary method of preparing BMG matrix composite alloys was implemented in accordance with an embodiment of the invention. The materials used in preparing the alloys were metals of high purity: copper (99.999%), aluminum (99.999%), tantalum (99.995%), niobium (99.995%), and a zirconium crystal bar with < 300 parts per million (ppm) oxygen content. Alloys of the composition  $(\text{Zr}_{70}\text{Ni}_{10}\text{Cu}_{20})_{90-d}\text{Ta}_d\text{Al}_{10}$  were prepared, where d equaled 2, 4, 5, 6, 8, 10 or 12.

[0022] The different alloys were prepared by arc melting in a titanium-gettered argon atmosphere on a water cooled copper hearth. The different alloys were prepared through a two-step process: (1) the zirconium and tantalum were combined to create a metastable crystalline phase and melted together to produce a homogeneous master alloy ingot; and (2) the nickel, aluminum, and copper were then melted with the zirconium-tantalum master alloy ingot. The nickel, aluminum, and copper may first be combined together prior to their combination with the metastable crystalline phase. The heat used to melt the



elements into the BMG matrix composite alloy may include electric arc heating or induction heating. For each step, the ingot was melted and flipped four or five times to promote homogeneity.

[0023] The final ingot was then cast into a copper mold to produce rods three millimeters in diameter and five centimeters in length. The casting may be accomplished through permanent mold casting, suction casting, injection die casting, pour casting, planar flow casting, melt spinning, or extrusion.

[0024] The metastable crystalline phase may be annealed, to precipitate particles, prior to combination with the other elements. Doing so may control: (1) the size of the precipitated particles; (2) the volume fraction of the precipitated particles; and/or, (3) the shape of the precipitated particles. Alternatively, the metastable crystalline phase may be a solid solution supersaturated in one or more elements at either ambient or an elevated temperature. Instead, the metastable crystalline phase may include a crystalline microstructure formed at an elevated temperature and retained at ambient temperature by rapid cooling. The crystalline particles may be stable in contact with the liquid alloy prior to casting. It should be appreciated that the crystalline particles have a melting temperature significantly higher than that of the remainder of the BMG matrix composite alloy. After casting, the alloy can be additionally shaped by molding or pressing at a temperature above, at or just below the glass transition temperature of the BMG matrix composite alloy.

[0025] The phases present in the as-cast samples were examined with X-ray diffraction (XRD) using a Rigaku TTRAXS  $\theta/\theta$  rotating anode diffractometer with Cu K $\alpha$  radiation

( $\lambda = 0.154 \text{ nm}$ ). The microstructure was examined using a Phillips CM300 field emission transmission electron microscope (TEM) and a JEOL 8600 Microprobe. The thermal properties of the composite samples were measured in a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC). Quasi-static compression tests were performed using a MTS servohydraulic machine.

[0026] The diffraction patterns for  $(\text{Zr}_{70}\text{Ni}_{10}\text{Cu}_{20})_{90-d}\text{Ta}_d\text{Al}_{10}$  (where  $d = 6$  and  $12$ ) are shown in Figure 1. The diffraction patterns indicate a broad scattering feature at  $38^\circ 2\theta$  along with sharp Bragg peaks corresponding to a crystalline phase. The broad scattering feature is consistent with an amorphous phase, in this case the matrix of the composite. The sharp Bragg peaks are identified as body-centered cubic tantalum. No other crystalline peaks can be seen in the diffraction patterns. Additionally, it can be seen that the scattering intensity of the tantalum peaks increases with an increasing atomic percentage of tantalum in the alloy. This indicates that the volume fraction of crystalline tantalum in the two-phase microstructure increases with increasing tantalum concentration.

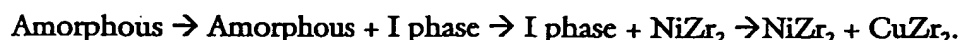
[0027] The as-cast composite microstructure for a ten percent tantalum alloy is shown in the optical micrograph in Figure 2. The microstructure consists of homogeneously dispersed particles (dark phase) in an amorphous matrix (light phase). The particles are oblong in shape but do not appear to possess a dendritic structure. The average size of the particles is approximately  $30 - 40 \text{ }\mu\text{m}$ . An electron microprobe determined the average chemical composition of the crystalline particles to be  $\text{Ta}_{93.2}\text{Zr}_{5.4}(\text{Cu}+\text{Ni}+\text{Al})_{1.4}$  (all compositions are in atomic percent). Optical micrographs for as-cast samples containing 4,

6, 8, 10, and 12 atomic percent of tantalum were examined. For the alloy containing 4% tantalum, there are no detectable precipitates in the optical micrographs. This would indicate that the tantalum solubility in the amorphous matrix is approximately 4%. The solubility of tantalum in the matrix was further examined by measuring the chemical composition of the matrix for the 4, 6, and 10 atomic percentage of tantalum alloys with an electron microprobe. Figure 3 shows the results of the matrix composition measurements along with the tantalum particle volume fraction measurements. It can be seen in Figure 3 that the volume fraction of the tantalum-rich particles present in the amorphous matrix scales linearly with the tantalum content in the alloy. This indicates that the microstructure can be tailored readily through variations in the alloy composition. Additionally, the microprobe results indicate that the amorphous matrix contains slightly less than 4% tantalum as predicted based on the volume fraction measurements.

[0028] To further confirm that the microstructure consists of crystalline tantalum-rich particles in an amorphous matrix, the matrix phase was examined using high-resolution transmission electron microscopy (HRTEM). The HRTEM image of the matrix shown in Figure 4 shows no evidence of lattice fringes, which would be associated with a crystalline structure. This is consistent with the X-ray diffraction patterns, which show no evidence of long-range order other than the crystalline tantalum-rich particles. Thus, the matrix surrounding the particles is amorphous.

[0029] The thermal properties of the amorphous matrix were examined using differential scanning calorimeter (DSC) analysis. The constant rate DSC scans for the 6

and 12% tantalum alloys are shown in Figure 5. To determine the crystallization sequence for the alloys, isothermal DSC was performed and the resulting microstructures were examined with X-ray diffraction. The XRD pattern for the 6% tantalum alloy, which had been annealed through the first exothermic peak, is shown in Figure 6. The annealed sample shows the crystalline tantalum peaks with additional sharp Bragg peaks corresponding to another crystalline phase. Using Bancel's indexing method, the peaks were found to be consistent with the formation of icosohedral quasicrystals (I phase). Further annealing of the sample resulted in the transformation of the icosohedral phase into the  $\text{NiZr}_2$  crystalline phase, which indicates that the quasicrystals are metastable. Figure 7 shows the XRD patterns for the annealed samples. When the samples were annealed through the last exothermic peak, the diffraction peaks associated with the quasicrystals disappeared and the intensity of the  $\text{NiZr}_2$  peaks were greatly reduced in intensity while the predominant phase present in the microstructure appeared to be the newly nucleated  $\text{CuZr}_2$  phase. Therefore, at higher temperatures, the  $\text{CuZr}_2$  phase appears to be the most stable and crystallization sequence can be represented as follows:



[0030] The mechanical properties of the alloy series were examined via quasi-static compression testing. Following ASTM standards, the samples tested had a length-to-diameter ratio of two to one. Figure 8 shows the compressive stress-strain curve for the as cast 8% tantalum alloy under quasi-static loading (strain rate  $\sim 10^{-4} \text{ s}^{-1}$ ). The specimen

exhibited an exceptionally large enhancement in the plastic strain prior to failure relative to monolithic metallic glasses of similar composition, which typically show 1 – 2 percent plastic strain before failure. The composite alloys tested here showed up to 15 percent total plastic strain prior to failure. The compressive tests also show that the large elastic elongation and high yield strength associated with the amorphous phase were largely unchanged.

[0031] In accordance with a preferred embodiment of the invention, the alloy possesses the proper characteristics and physical attributes to make it desirable for various civilian and military applications, such as in the aerospace, transportation and sporting goods industries (e.g., golf club heads). For example, the high strength, good compressive ductility and potentially good fracture toughness make use the composite material promising as a kinetic energy penetrator in armor-piercing projectiles. Other potential applications for the novel alloy include springs and other compliant mechanisms.

[0032] While preferred embodiments of the invention have been described in detail herein, it should be readily understood that the invention is not limited to such disclosed embodiments. Rather, disclosed embodiments can be modified to incorporate any number of variations, alterations, substitutions or equivalent arrangements not heretofore described, but which are commensurate with the spirit and scope of the invention. Accordingly, the invention is not to be seen as limited by the foregoing description, but is only limited by the scope of the appended claims.

[0033] What is claimed as new and desired to be protected by Letters Patent of the United States is:

## CLAIMS

1. An alloy formed of a bulk metallic glass matrix with a microstructure of crystalline metal particles, the alloy having a composition of  $(X_aNi_bCu_c)_{100-d-e}Y_dAl_e$ , wherein the sum of a, b and c equals 100, wherein  $40 \leq a \leq 80$ ,  $0 \leq b \leq 35$ ,  $0 \leq c \leq 40$ ,  $4 \leq d \leq 30$ , and  $0 \leq e \leq 20$ , and wherein X comprises an early transition metal and Y comprises a refractory body-centered cubic early transition metal.
2. The alloy of claim 1, wherein X comprises one or more early transition metals chosen from a group consisting of zirconium, hafnium, and titanium.
3. The alloy of claim 1, wherein Y comprises one or more refractory body-centered cubic early transition metals chosen from the group consisting of molybdenum, niobium, tantalum, tungsten and vanadium.
4. The alloy of claim 1, wherein the microstructure of crystalline metal particles comprises one or more from the group consisting of early transition metal and the refractory body-centered cubic early transition metal.
5. The alloy of claim 4, wherein the microstructure of crystalline metal particles comprises tantalum.
6. The alloy of claim 4, wherein the microstructure of crystalline metal particles comprises tantalum and zirconium.

7. The alloy of claim 1 having a composition of  $Zr_{58.8}Ni_{8.4}Cu_{16.8}Ta_6Al_{10}$ .
8. The alloy of claim 1 having a composition of  $Zr_{57.4}Ni_{8.2}Cu_{16.4}Ta_8Al_{10}$ .
9. The alloy of claim 1 having a composition of  $Zr_{56}Ni_8Cu_{16}Ta_{10}Al_{10}$ .
10. The alloy of claim 1 having a composition of  $Zr_{54.6}Ni_{7.8}Cu_{15.6}Ta_{12}Al_{10}$ .
11. The alloy of claim 1, wherein the metallic glass matrix is at least partially crystalline.
12. The alloy of claim 1, wherein the metallic glass matrix is at least partially quasi-crystalline.
13. The alloy of claim 1, wherein the plastic strain to failure in uniaxial compression at ambient temperature is greater than five percent.
14. The alloy of claim 1, wherein the plastic strain to failure in uniaxial tension at ambient temperature is greater than two percent.
15. The alloy of claim 1, wherein the average grain size of said crystalline metal particles is between about 0.1 microns and about 100 microns.



16. The alloy of claim 1, further comprising as an additional element at least one of niobium and titanium, wherein said additional element reacts readily with impurities to improve glass-forming ability of the alloy.

17. A method of producing an alloy comprising two or more phases at ambient temperature, comprising the steps of:

providing a metastable crystalline phase comprising at least two elements;

heating the metastable crystalline phase together with at least one additional element to form a liquid with suspended particles of a crystalline phase;

casting the liquid; and

cooling the liquid to form the alloy;

wherein said providing includes controlling composition of the liquid.

18. The method of claim 17, wherein the controlling of the composition of the liquid determines a volume fraction of the metastable crystalline phase.

19. The method of claim 17, wherein said heating comprises heating the metastable crystalline phase together with at least two additional elements, the additional elements being combined with each other prior to the heating step.

20. The method of claim 17, further comprising annealing the metastable crystalline phase prior to said heating step.

21. The method of claim 17, wherein said heating comprises electric arc heating.
22. The method of claim 17, wherein said heating comprises induction heating.
23. The method of claim 17, wherein said casting comprises one of the group consisting of permanent mold casting, suction casting, injection die casting, pour casting, planar flow casting, melt spinning, and extrusion.
24. The method of claim 17, further comprising shaping the alloy at a temperature above, at or just below the glass transition temperature of the solid alloy.
25. The method of claim 17, wherein the alloy has a composition of  $((\text{Zr}, \text{Hf})_a\text{Ni}_b\text{Cu}_c)_{100-d-e}\text{Ta}_d\text{Al}_e$ , where  $a + b + c$  equals 100,  $40 \leq a \leq 65$ ,  $0 \leq b \leq 10$ ,  $0 \leq c \leq 20$ ,  $4 \leq d \leq 30$ , and  $0 \leq e \leq 15$ .
26. A method of producing an alloy comprising two or more phases at ambient temperature, comprising the steps of:
  - providing a metastable crystalline phase comprising at least two elements;
  - heating the metastable crystalline phase together with at least one additional element to form a liquid;
  - casting the liquid; and

cooling the liquid alloy at a cooling rate to form the alloy;  
wherein the cooling rate is controlled.

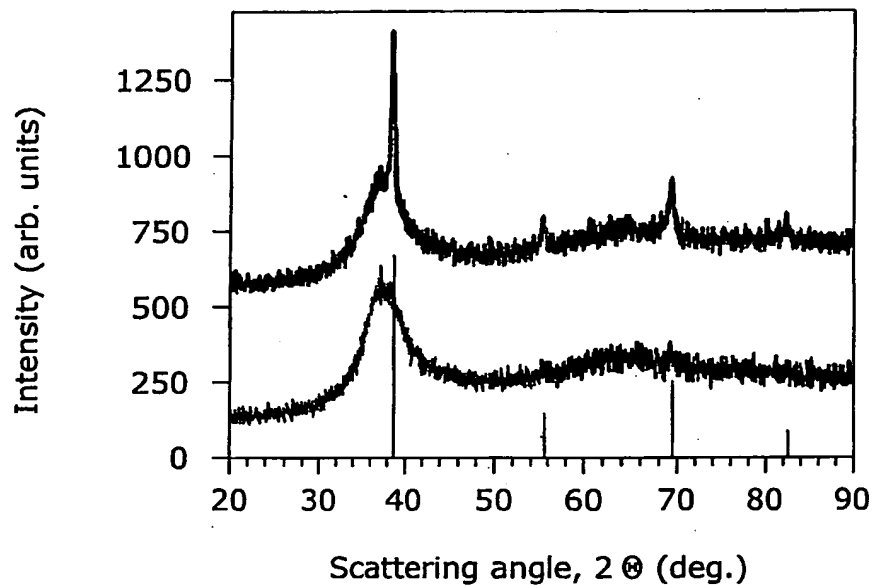
27. The method of claim 26, wherein the controlling of the cooling rate controls the average size of crystalline particles in the metastable crystalline phase.

28. The method of claim 27, wherein the average size of the crystalline particles in the metastable crystalline phase are between about 10 microns and about 50 microns.

29. The method of claim 26, further comprising the step of controlling composition of the liquid.

30. The method of claim 26, further comprising annealing the metastable crystalline phase.

1/5

**Fig. 1**

X-ray diffraction pattern showing the phases present in a 6 % Ta alloy (bottom) and a 12 % Ta alloy (top). In both cases, there are sharp diffraction peaks indicative of body-centered-cubic (bcc) Ta (solid lines), plus a broad scattering feature near 37° characteristic of an amorphous phase.

2/5

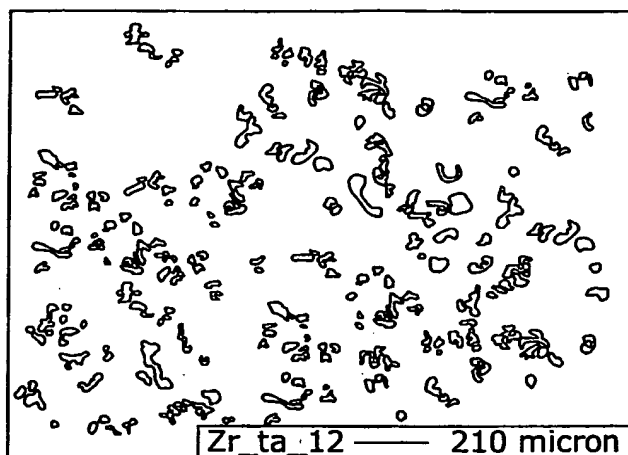


Fig. 2

Optical micrograph of a polished sample of  $\text{Zr}_{55}\text{Ni}_8\text{Cu}_{15}\text{Ta}_{12}\text{Al}_{10}$ . The microstructure consists of an amorphous metallic matrix, with 20-50 micron diameter precipitates of a Ta-rich crystalline phase.

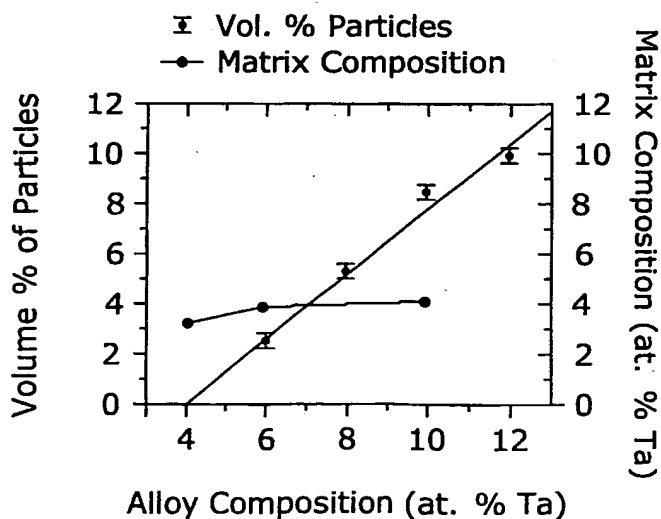


Fig. 3

Plot of volume fraction of the crystalline phase and Ta concentration in the amorphous matrix as a function of overall Ta content in the alloy. The volume fraction of crystalline precipitates increases linearly with Ta concentration, indicating ability to control the microstructure of the alloy.

3/5

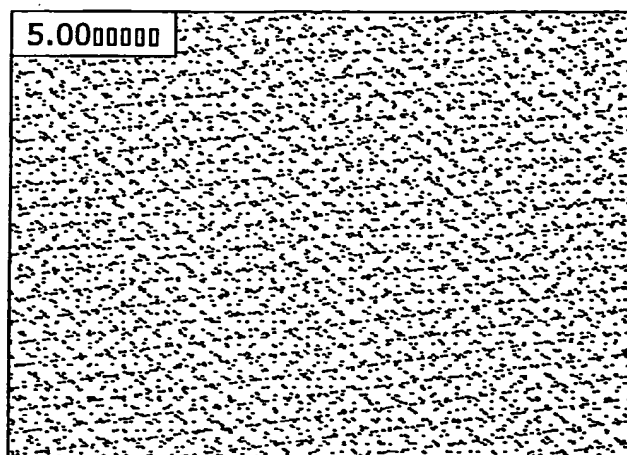


Fig. 4

HTREM image of matrix for a 5 % Ta alloy. The amorphous structure of the matrix is confirmed by the absence of lattice fringes.

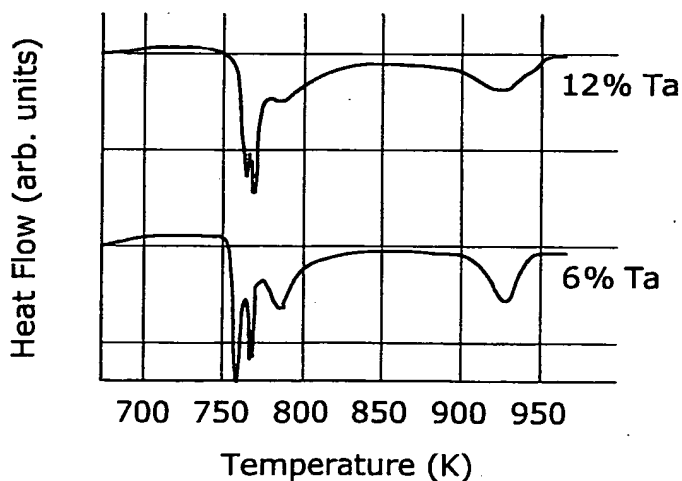
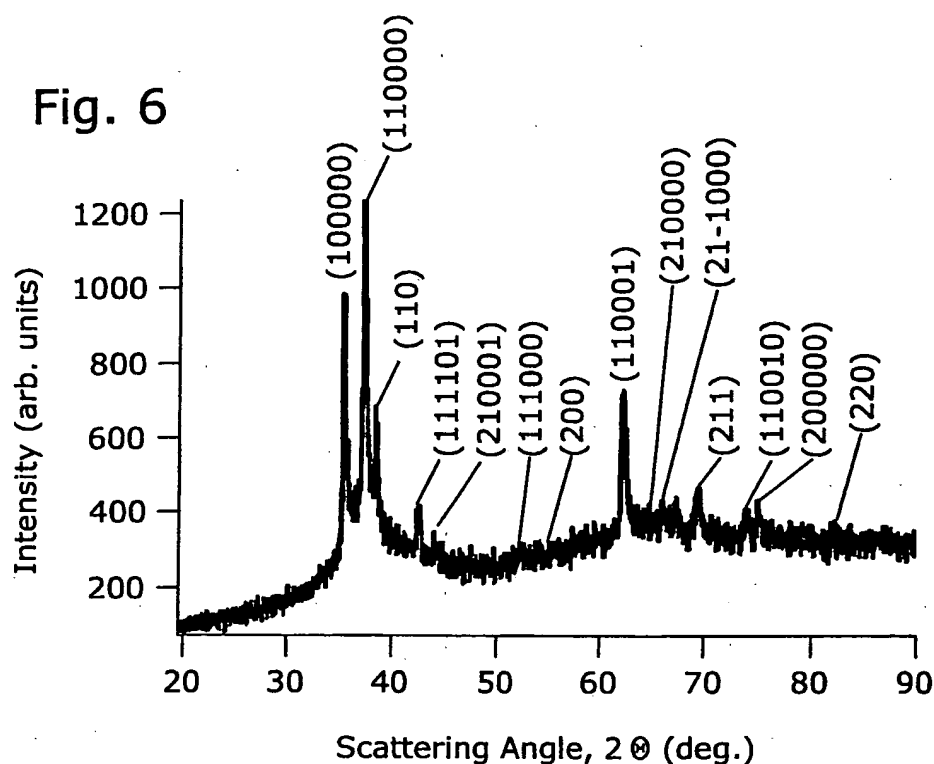


Fig. 5

Differential scanning calorimetry (DSC) traces from a 6 % Ta alloy and 12 % Ta alloy. Note the distinct glass transition temperature at approximately 700K, which is additional confirmation that the matrix is a metallic glass.

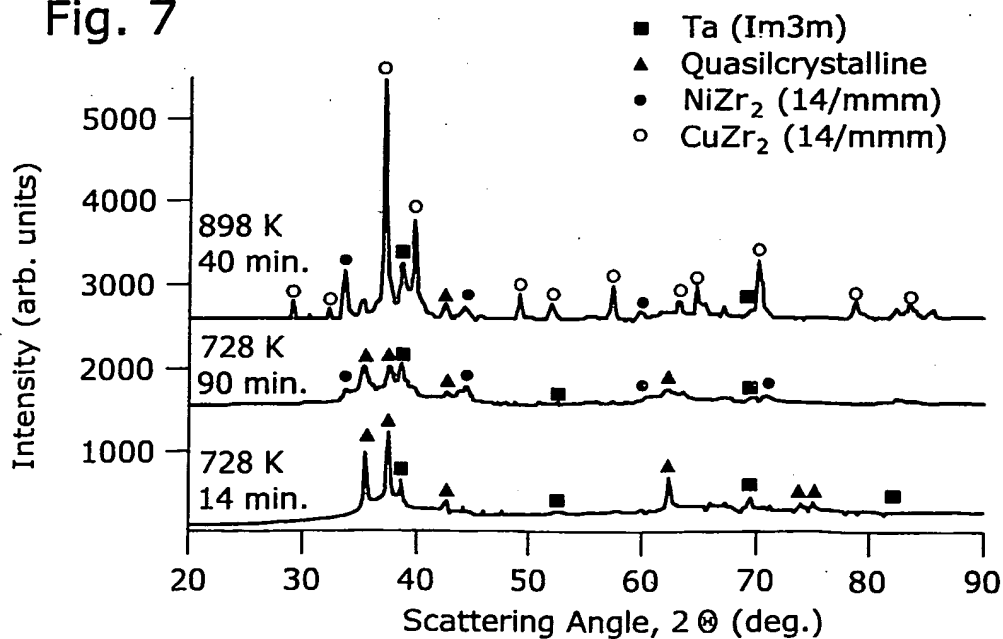
4/5

Fig. 6



X-ray diffraction pattern showing evidence for a quasicrystalline phase present in 6% Ta alloy that has been annealed at 728 K for 14 minutes.

Fig. 7



X-ray diffraction patterns for a 6% Ta alloy showing the phases present after isothermal annealing for the temperatures and times indicated.

5/5

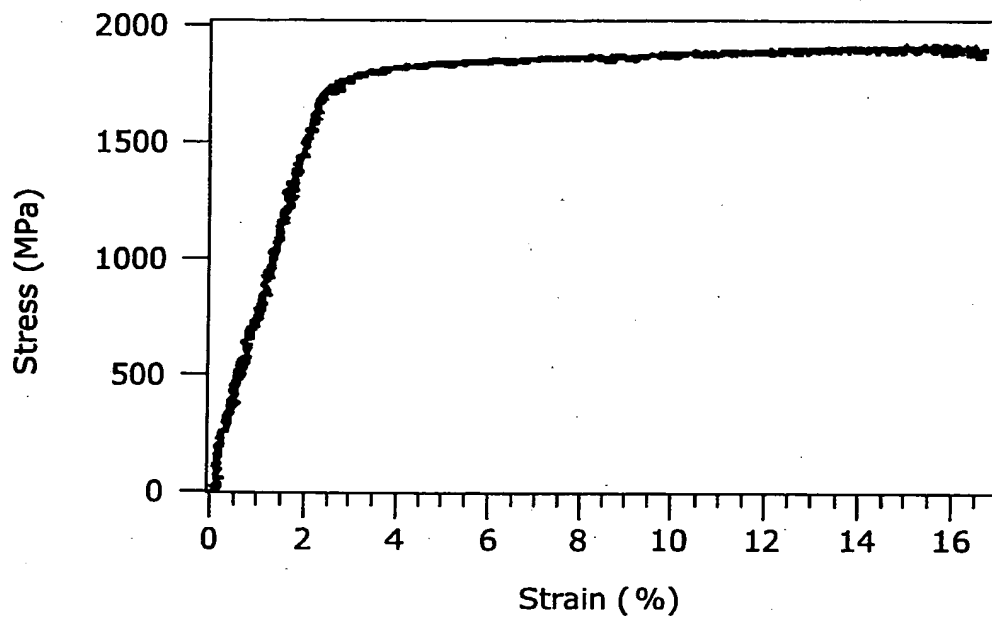


Fig. 8

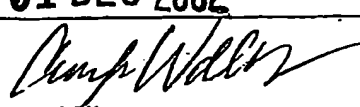
Stress-strain curve for a 8% Ta alloy. Note the high flow strength (1.9 GPa), apparent work hardening, and the extended region of plastic deformation (14% plastic strain to failure).



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/35436

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : C22C 45/10; B22D 23/06 US CL : 148/561, 403; 164/80, 113, 312 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 148/561, 403; 164/80, 113, 312 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WBST		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,711,363 A (SCRUGGS et al.) 27 January 1998 (27.01.1998), Figure 3 and entire document.	17-24, 26-30
Y	US 5,740,854 A (INOUE et al.) 21 April 1998 (21.04.1998), columns 3-6.	17-24, 26-30
A		1-16, 25
Y	US 6,267,171 A (ONUKI et al.) 31 July 2001 (31.07.2001), column 1.	17-24, 26-30
Y	US 6,258,185 A (BRANAGAN et al.) 10 July 2001 (10.07.2001), columns 4-7.	17-24, 26-30
A		1-16, 25
Y	US 4,144,058 A (CHEN et al.) 13 March 1979 (13.03.1979), columns 2-5.	17-24, 26-30
A		1-16, 25
A,P	US 6,427,753 B1 (INOUE et al.) 06 August 2002 (06.08.2002), entire document.	1-30
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 09 December 2002 (09.12.2002)		Date of mailing of the international search report <b>31 DEC 2002</b>
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230		Authorized officer Thomas Dunn  Telephone No. 703-308-0661

**INTERNATIONAL SEARCH REPORT**

PCT/US02/35436

**C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RE 32,925 A (CHEN et al.) 16 May 1989 (16.05.1989), entire document.	1-30
A	WO 00/68469 A2 (CALIFORNIA INSTITUTE OF TECHNOLOGY) 16 November 2000 (16.11.2000), entire document.	1-30